

Synchrotron Studies of Amiphiphiles with Crown Polar Heads at Air-Water Interface

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INTRODUCTION

Interfacial behavior of amiphiphilic monodendrons with photochromic properties is an intriguing topic in the field of tunable organized molecular films. The mismatch of cross-sectional areas for polar heads and dendritic shells with multiple alkyl-terminated branches determines their non-trivial packing structure and physical behavior of monolayers at solid and liquid surfaces (see sketch in Figure 1).^{1,2} Recently, we have proposed using bulky polar heads to balance dendritic shells and observed that the photochromic behavior of the Langmuir monolayers was, in fact, controlled by this cross-sectional mismatch.^{3,4} The initial formation of organized intralayer packing at the air-water interface is a key stage which governs their solid state properties. In the present communication, we report on preliminary results of synchrotron studies of amiphiphilic photochromic molecules with bulky polar head such as presented in Figure 1. The molecules with more than one tail are currently under investigation.

RESULTS AND DISCUSSION

The **AD12-1** molecule presented in Figure 1, consists of a large crown ether head attached to a photochromic azobenzene group and has a single twelve carbon alkyl tail attached to the opposite end of the azobenzene. The synthesis involved was previously described.³ The monolayers were prepared from a chloroform solution with a concentration of 1.0 mmol/L. A typical π -A isotherm is shown in Figure 2. Molecular modeling using Cerius² package shows a cross-sectional area of the polar head of 45 Å² while it is known that a single alkyl tail has a cross-sectional area of about 20 Å².⁵ As clearly seen in the isotherm, the large polar head controls the packing of the molecules.

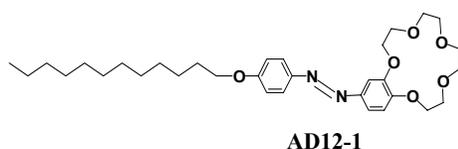


Figure 1. General scheme of amiphiphilic monodendrons (left) and chemical structure of the **AD12-1** molecule with bulky crown-ether head, central photochromic group, and one alkyl tail (right).

X-ray grazing incident diffraction (XGID) and reflectivity measurements⁶⁻⁸ were conducted on a liquid-surface X-ray spectrometer at the 6ID beamline at the Advanced Photon Source synchrotron at Argonne National Laboratory as described elsewhere. The wavelength during the experiments was selected at 0.772 Å. A Langmuir trough was placed in a helium environment to reduce the background scattering from air and prevent oxidation reaction that can damage the monolayer. The monolayer was compressed at a rate of 1.2 Å²/min until the desired pressure was reached. The subphase was Nanopure water at 18°C.

Reflectivity and XGID data were gathered at three surface pressures shown on Figure 2. After compression the monolayer was held at that pressure for the duration of the measurements.

Figure 3 shows the XGID scan from monolayer at 18 mN/m. XGID scans detected three peaks at surface pressures higher than 10mN/m. The XGID pattern was fitted to Lorentzian type curves with the peak positions at 1.00, 1.43, and 1.59 Å⁻¹, corresponding to 6.26, 4.40, and 3.94 Å d-spacings, respectively. The two peaks with higher Q_{xy} values corresponded with literature values for (1,1) and (2,0) planes in an orthorhombic unit cell of polyethylene.⁹ Calculations determined a unit cell size of 7.88 by 5.29 Å, which gave the cross-sectional area of 20.8 Å² per alkyl chain of the molecule. This value is within the known area for densely packed and tilted alkyl tails.^{5,9}

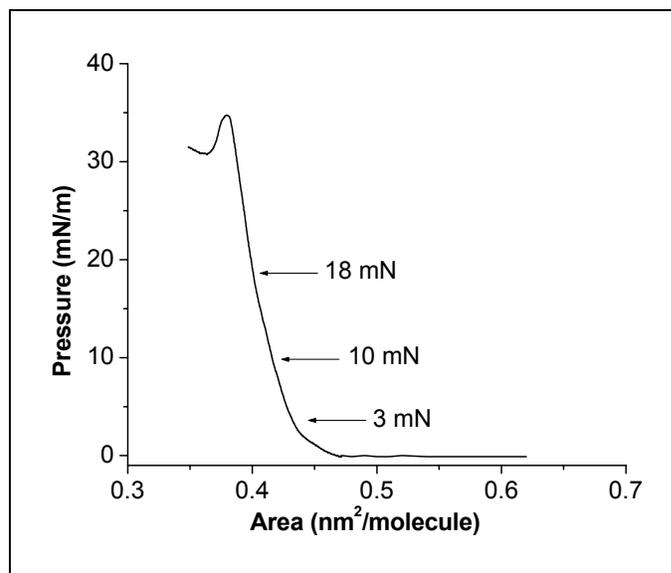


Figure 2. π -A isotherm for **AD12-1**. The surface pressures used in the X-ray experiments are labeled.

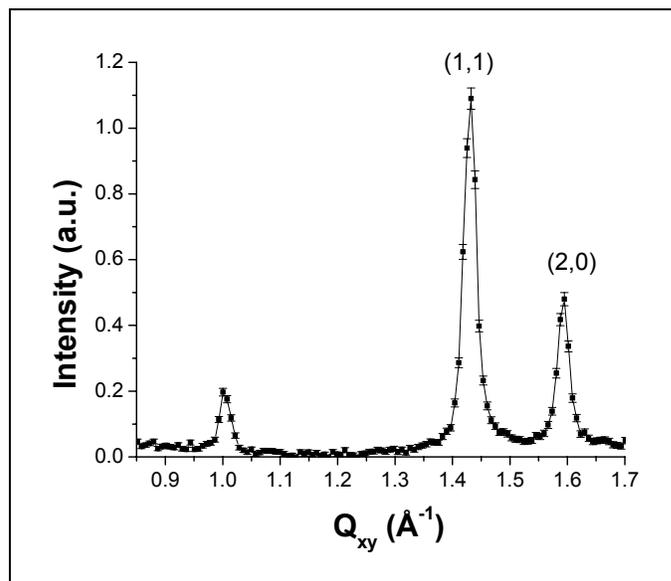


Figure 3. XGID scan of the **AD12-1** monolayer at higher surface pressure. Characteristic peaks for the (1,1) and (2,0) planes are labeled.

Data from the rod scans supports the idea of molecules tilting in a preferred direction. We suggest that the additional peak at $d = 6.26 \text{ \AA}$ corresponds to the dense packing of polar heads.

The box model¹⁰ was used to fit the data shown in Figure 4 for the **AD12-1** monolayer at higher surface pressure. The first box, corresponding to the azobenzene and polar head has a length of 12.9 \AA and an electron density of 0.41 e/\AA^3 while the second box associated with the alkyl tails has a length of 7.5 \AA and an electron density of 0.24 e/\AA^3 . The distinction between the polar head and photochromic azobenzene fragment cannot be resolved within current resolution. The length of the topmost box indicates that the tails are tilted toward the surface. The angle is estimated at 60° from the surface normal. The density of the tails extracted from the model is lower than the expected electron density of densely packed alkyl tails, which suggests the domain microstructure of the monolayer.

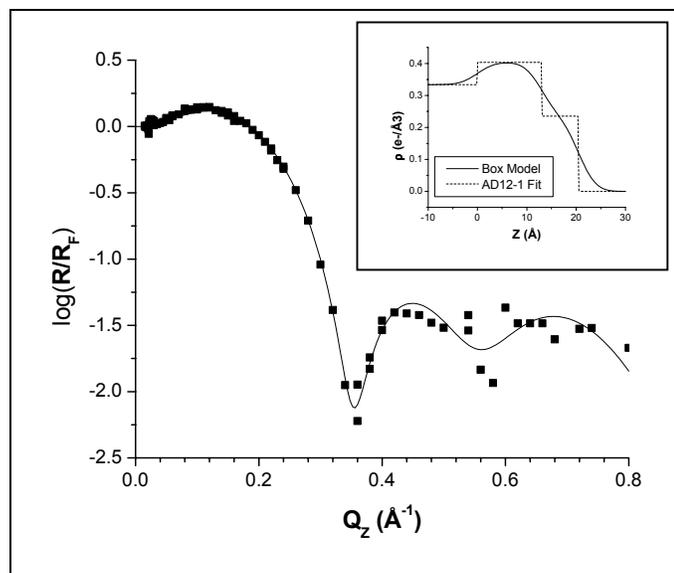


Figure 4. Reflectivity data for the **AD12-1** monolayer at higher surface pressure: squares are experimental data, solid line is simulation for model electron density. The insert shows two-box model and corresponding smeared electron density distribution along the normal to the surface plane.

In conclusion, X-ray scattering of photochromic amphiphilic molecules at the air-water interface demonstrated that under higher surface pressure a dense packing of the alkyl tails was formed with highly tilted tails and ordering that can be approximated with two-layer density model.

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